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OFFICE OF  
PREVENTION, PESTICIDES, AND  
TOXIC SUBSTANCES

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**MEMORANDUM**

**SUBJECT:** Review of Interim Report on the Results From the 2007 Atrazine Ecological Monitoring Program (MRID# 47295002) and Recommendations for Monitoring for 2008

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OPP has reviewed Syngenta's 2007 interim report, which is an addendum to the 2004-2006 report on the Atrazine Ecological Exposure Flowing Water Chemical Monitoring Study in Vulnerable Watersheds (MRID 47174102). This interim report provides results from additional monitoring conducted for one of the following reasons:

- Triggered the LOC in multiple years: MO-01 & MO-02 , along with additional sites (MO-04a and -04b, MO-05) in adjacent subwatersheds
- Exceeded LOC in 1 year: IN-11
- Low rainfall during the planting period in 1 or more years: IL-03, IL-04, IL-08, IN-06, OH-02 [IN-11 also qualified in this category]

## **Recommendations Regarding Continued Monitoring and Decommissioning**

Based on a review of the interim data submitted by Syngenta, OPP recommends continued monitoring in the MO sites as part of the mitigation efforts, additional monitoring in 3 NE sites (NE-04, NE-05, and NE-07) which experienced sampling problems due to low flow conditions, and an additional year of monitoring in IN-11 due to continued unusually low rainfall conditions during the critical planting window. Rationales are briefly explained below, with additional supporting information supplied in sections that follow.

- (1) Continue monitoring the Missouri sites using the modified sampling approach implemented in 2007 (mix of grab and autosamples). Because these sites exceeded the LOC in multiple years, the monitoring efforts have shifted from determining whether the sites exceed the LOC as a part of a survey to assessing the effectiveness of public outreach, stewardship, and other efforts in reducing atrazine loading in the waterbodies. Continued monitoring in those watersheds should focus on these questions:
  - How well is the current outreach and stewardship program working?
  - Are reductions in atrazine loads evident over time in MO-01 and MO-02?
  - Do additional areas of concern exist within the larger HUC-10? Syngenta is addressing this question with monitoring in MO-04a and b and MO-05.
- (2) Re-establish monitoring at the three NE sites (NE 04, NE 05, and NE 07) that experienced low flow conditions which precluded sampling during portions of the monitoring seasons in 2005 and 2006. While OPP did not request follow-up sampling at these sites in 2007, further examination of the data and feedback from the December 2007 SAP indicate that additional monitoring is warranted.

While reports submitted by Syngenta indicate that, in a few instances, samples were not taken because the streams were dry, in most instances missing samples were attributed to "low flow" conditions. In some cases, the autosampler collected data on days when no grab samples were obtained because of low flow. By OPP's estimates, all 3 sites potentially exceeded the LOC in at least 1 year.

Because of uncertainties both in terms of actual flow conditions during the monitoring study and what is represented by intermittent flow conditions, the SAP recommended further evaluation of these sites. The SAP recommended "alternative sampling methods that do not require streams to be at least 5 inches deep" [SAP Minutes No. 2008-01, p. 32]. Syngenta needs to design a sampling approach that collects samples when water is present in the stream, no matter how shallow. The modified sampling approach used in 2007 (including both 4-day grab samples and autosamplers) should be employed here, with all additional efforts taken, as necessary, to collect samples when water is present in the stream. Such efforts

should not preclude manually collecting samples from the streams if the depth is too shallow for the grab sample devices to collect from the bridge,

Uncertainties and misunderstandings in interpreting results of these sites point to the need for more detailed information on stream stage (depth) and flow for each site than was provided in previous submissions. This includes more information on baseline elevation, stream stage, condition of the stream at the time of sampling, and detailed descriptions of the tools and methods used to measure stream stage.

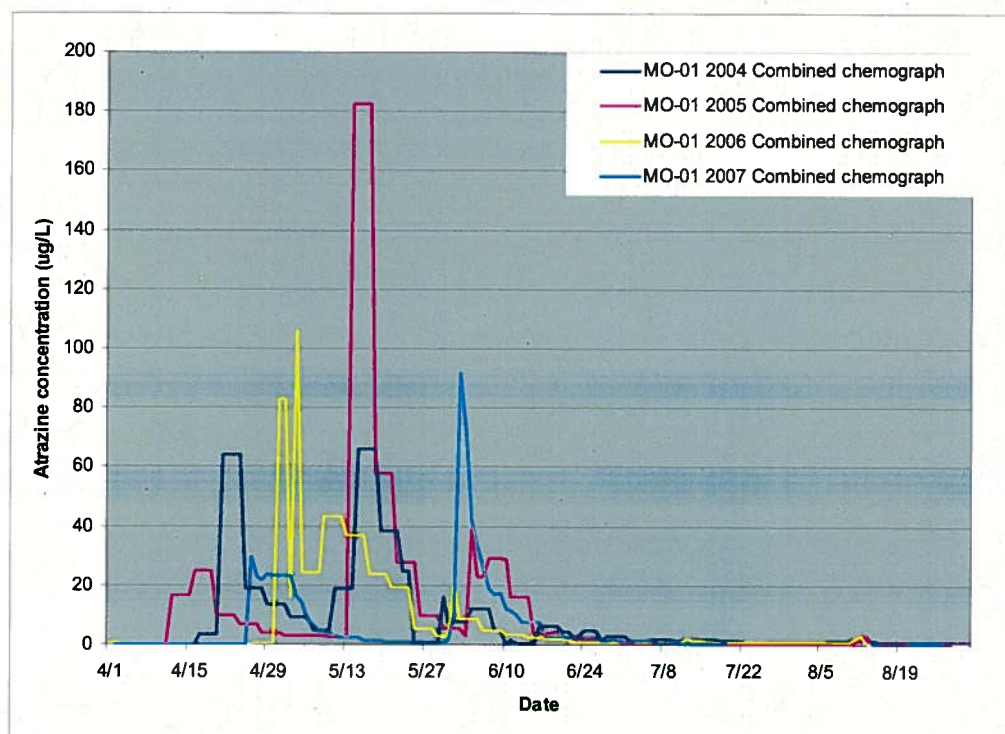
In addition, the SAP recommended assessing the watersheds for any potential upstream agents that might be causing the low-flow conditions [SAP Minutes No. 2008-01, p. 29]. OPP noted a drastic dropoff in corn acreage in NE-07 in 2006, based on USDA NASS cropland coverage, potentially due to a three-year (or more) crop rotation. The extent of the watershed in corn should be quantified as a part of the monitoring program for each year of existing and future monitoring.

- (3) OPP will not request further monitoring in the five watersheds that included a third year of monitoring in 2007:
- Three sites (IL-04, IL-08, IN-06) did not exceed the LOC in 2007 with rainfall closer to historically typical averages during and immediately after the planting season.
  - Two sites (IL 03, OH 02) still had low rainfall during the planting season, but experienced runoff events in the planting window that did not result in exceedances of the LOC.
- (4) An additional year of monitoring had been requested for the IN-11 because it exceeded the LOC in the first year and because it experienced years with abnormally low (2005) and high (2006) rainfall during the sampling period. While results from monitoring in 2007 did not exceed the LOC, the site experienced such unusually low rainfall – among the lowest rainfall totals in the 42 years of historical data provided for the site, with few or no rainfall events recorded during the planting window – that it is difficult to interpret the results in terms of the potential for atrazine exposure during a more typical rainfall year. OPP requests that monitoring be continued in IN-11 for an additional year.

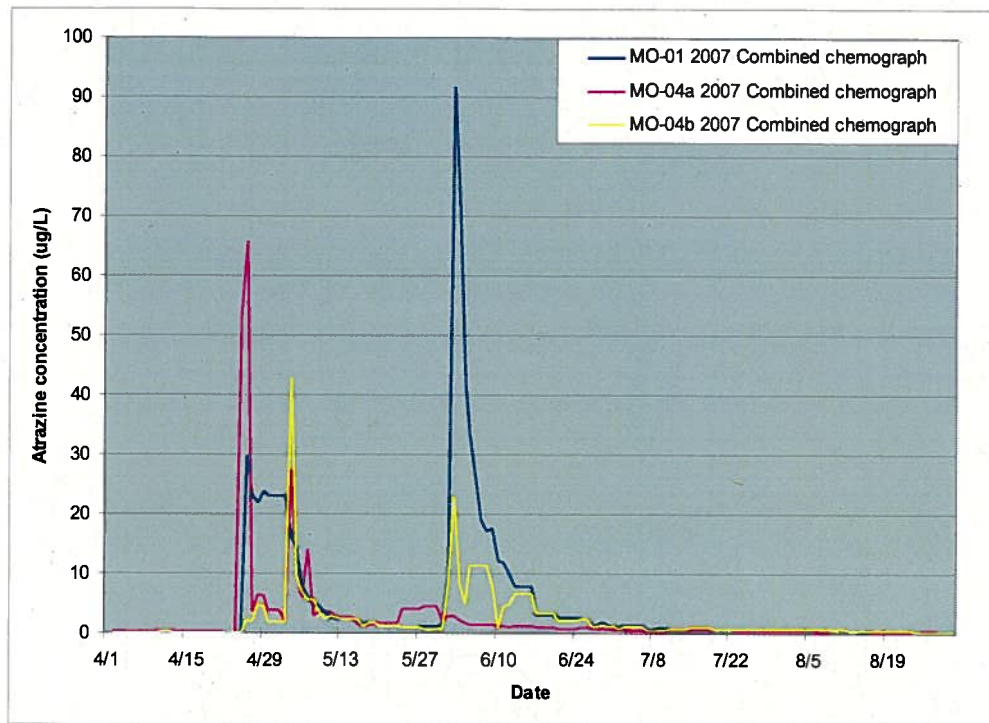
### **Evaluation of Continued Monitoring in MO**

Both MO-01 and MO-02 have triggered the LOC and are in a phase similar to a TMDL implementation program. In 2006-07, Syngenta started an outreach program in the watersheds in MO-01 and MO-02. They added monitoring in adjacent subwatersheds – MO-04a and b (adjacent to MO-01) and MO-05 (adjacent to MO-02) – to evaluate the potential for LOC exceedances in other subwatersheds within the larger HUC-10 watershed.

None of the chemographs for the Missouri sites exceeded the LOC using the CASM\_Atrazine model presented to the December 2007 SAP. The peak concentration for MO-01 in 2007 (91.6 ug/L) was in the same magnitude as detections in 2004 and 2006, but the combined magnitude and duration of exposure in 2007 was less than in previous years (Figure 1). Both peak concentrations and durations of exposure in MO-04a and 04b were less than the peak detection in MO-01 (Figure 2).



**Figure 1 - Chemographs for MO-01, 2004-07**

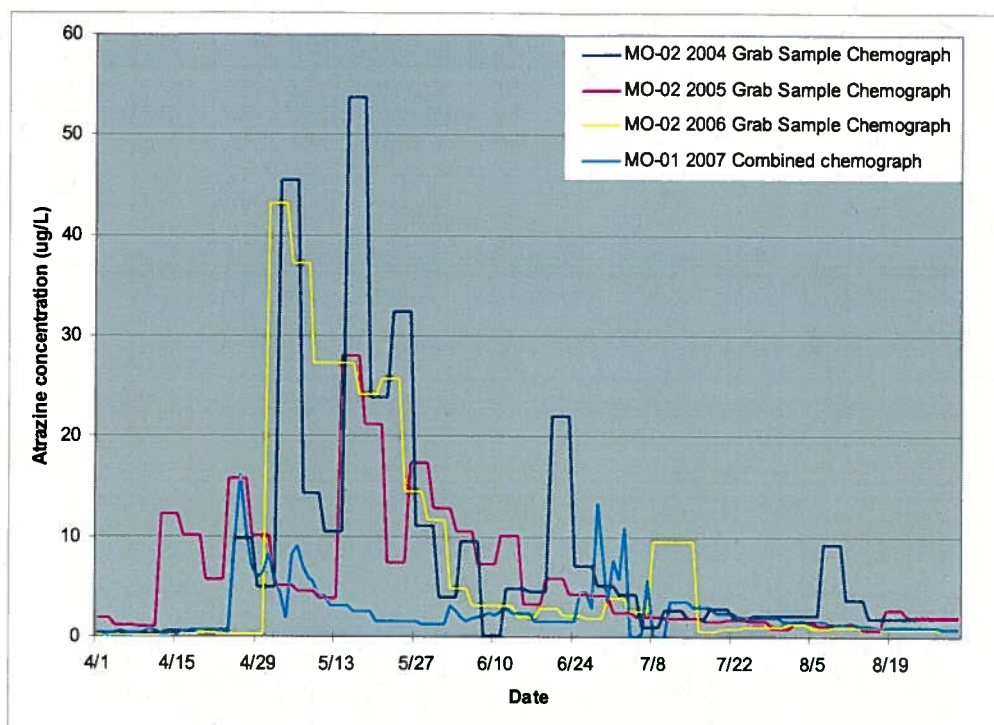


**Figure 2 - Chemographs for MO-01, -04a, and -04b in 2007**

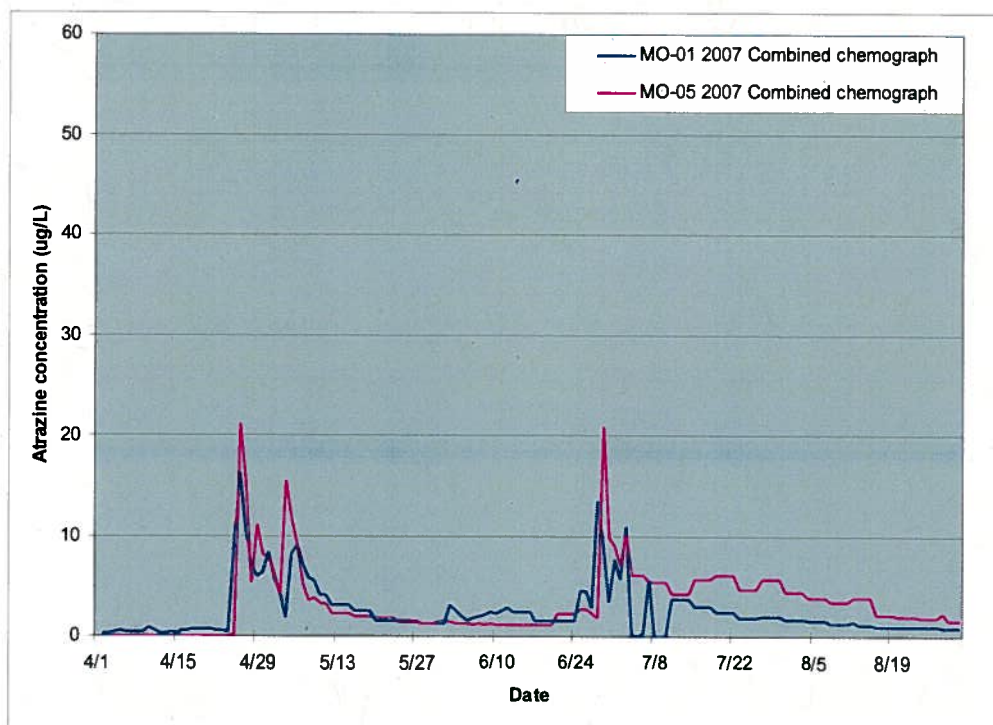
Atrazine concentrations detected at the MO-02 site in 2007 were lower than detections in previous years (Figure 3). Concentrations in MO-05 were similar, but slightly higher (exceeding 20 ug/L on 2 occasions) than those measured at the MO-02 site in 2007 (Figure 4).

It is difficult to determine whether the results of the 2007 monitoring at the MO sites reflect a reduction in atrazine loads as a result of Syngenta's public awareness efforts, differences in weather patterns from year to year, or shifts in corn acreage as a result of crop rotations. Such conclusions will require additional monitoring and subwatershed-scale evaluations of land use patterns, cropping practices, atrazine use, and stewardship efforts.





**Figure 3 - Chemographs for MO-02, 2004-07**



**Figure 4 - Chemographs for MO-02 and -05 in 2007**

## Re-evaluation of Low or No Flow Sites in Nebraska

Three of the seven Nebraska sites reported “low, or no-flow” conditions resulting in a high number of missing samples in 2005 and 2006. All three low/no flow sites – NE-04, NE-05, and NE-07 – are located in southeastern Nebraska. In a closer evaluation of the data in preparation for the December 2007 SAP, EPA noted that most of the missing samples were attributed to low flow conditions and not dry streams. In addition, periods during which 4-day grab samples were missed sometimes included high atrazine exposures measured in autosamples. Syngenta's subsequent explanation during the 2007 SAP was that the low-flow dates were times when water was present in the streams but at a depth too shallow to be sampled using the grab sample device. The autosampler did not have the same depth limitations.

Based on this information, EPA integrated the autosample and grab sample measurements into a combined chemograph using these rules:

- Measured concentrations from either the grab sample or autosample represented that day and subsequent days between sample events. This is the same stairstep approach used by CASM\_Atrazine.
- On days when multiple samples (combination of grab and autosamples or more than one autosample) were taken, the highest concentration was used for that day.
- For autosamplers that included multiple concentrations measured over the course of the day, the last measured value was used for stairstep interpolation across subsequent days.
- Concentrations for missing samples from the regularly-scheduled 4-day grab sample events depended on the reported reason for the missing sample:
  - If no sample was taken because of low flow (or other sample-related glitch), concentrations from the last monitoring event (grab sample or autosample) were used.
  - If no sample was taken because of no flow, concentration was set to 0.
- If the reported concentrations was less than the LOQ, the concentration was set at the LOQ (this had no impact on the CASM\_Atrazine results).

NE-04 had the highest number of no-sample events because the stream bed was dry (11 sample dates in 2005, 19 in 2006). In 2005, the grab samples included 4 dates with low or no flow and 22 dates with detections ranging from 0.17 to 49.85 ug/L. In 2006, 19 sample dates had low flow, 1 had a nondetection, and 9 had detections ranging from 0.11 to 4.12 ug/L. However, the autosampler installed in 2006 included 18 additional dates with sample detections ranging from 0.14 to 122 ug/L, with 2 separate peaks above 120 ug/L. The combined chemographs resulted in %SSI values of 3.9% in 2005 and 6.5% in 2006, compared to the 4% LOC using the 2007 CASM\_Atrazine model.

No missing samples in NE-05 resulted from no flow/dry stream conditions in either year. In 2005, 12 sample dates were missed because of low flow and 1 because of a broken sampler. For the remaining samples, 2 had nondetects and 22 had detections ranging from 0.11 to 49.87 ug/L. In 2006, 25 dates had missing samples due to low flow, 7 had nondetects, and 8 had detections ranging from 0.13 to 6.76 ug/L. The autosampler installed in 2006 included 3 dates with detections ranging from 0.36 to 6.62 ug/L. The combined chemographs resulted in %SSI values of 4.6% in 2005 and 0.6% in 2006, compared to the 4% LOC using the 2007 CASM\_Atrazine model.

For NE-07, none of the missed samples in 2005 were the result of no flow/dry stream conditions. Eight of the missed samples in 2006 were attributable to no flow. In 2005, 8 grab sample dates were missed as a result of low flow while 5 dates had nondetects, and 24 had detections ranging from 0.17 to 112.19 ug/L. In 2006, 29 grab sample dates were missed because of low flow, 2 had nondetects, and only 1 had a detection (1.94 ug/L). However, the autosampler added in 2006 included 11 additional dates with detections ranging from 0.15 to 1.01 ug/L. The combined chemographs resulted in %SSI values of 5.2% in 2005 and 0.6% in 2006, compared to the 4% LOC using the 2007 CASM\_Atrazine model.

Several issues remain outstanding in interpreting the results from these three low-flow sites:

- (1) The December 2007 SAP indicated that, even if the 3 sites represent intermittent streams, they should be included as representative of a certain population within the larger pool of 1,172 vulnerable watersheds.
- (2) Further work should be done to determine whether the low- or no-flow nature of these streams is due to natural intermittent conditions or to artificial diversions upstream.
- (3) The information provided by Syngenta in its reports on these sites indicates that, while the missing samples were attributed to "no flow" or "dry stream bed" in some instances, particularly for NE-04, the majority of the missing samples resulted from "low flow", suggesting that while water was present in the stream, it was not of sufficient depth for the grab sample devices to capture a sample. Further, autosamplers added to the sites in 2006 obtained samples during periods when the grab samples did not.

These results indicate that further monitoring is necessary. In addition, Syngenta should provide a revised monitoring strategy that ensures that samples are taken when water is present in the streams. A monitoring strategy employing both grab samples and autosamplers, similar to what Syngenta did in the 2007 monitoring sites, may address this sampling issue. Field notes provided to OPP should be more specific in describing conditions present at the time of sampling.



## Evaluation of the Monitoring Sites Based on Weather

In 2007, OPP requested an additional year of monitoring at five sites which had one or more years of abnormally low rainfall (defined as at or below the 25<sup>th</sup> percentile in comparison to historical averages within the planting season) during the early sampling period. None of these sites had exceeded the LOC in either year of monitoring:

IL-03, IL-04, IL-08

IN-06

OH-02

Additionally, IN-11, which included a third year of monitoring because it exceeded the LOC in one year, also had both low and high rainfall years in its two years of sampling.

These sites represented a larger group of sites with one or more years of low rainfall:

IL-01 [2005], IL-02 [2005], IL-03 [2005-06], IL-04 [2005-06], IL-05 [2005], IL-06 [2005], IL-07 [2005], IL-08 [2005-06], IL-09 [2005], IN-02 [2005], IN-06 [2005], IN-11 [2005], KY-02 [2005], MN-01 [2006], OH-02 [2005], OH-03 [2005].

In addition to analyzing the atrazine chemographs using CASM-Atrazine, OPP evaluated rainfall patterns by first comparing monthly rainfall totals against historical averages from multiple years of local weather data. Secondly, OPP looked at measured rainfall during the sample year in relation to the reported planting seasons and to atrazine monitoring data. Results of the analysis are briefly summarized below.

In IL-03, atrazine concentrations were consistently low in all 3 years (<6 ug/L). The autosampler added in 2007 helped fill in detections related to rainfall events. Total rainfall was low in April (~25th %ile) and May (<10th %ile) of 2007, similar to previous years, and at or above normal in June through August. However, the planting period included four days with rainfall above 0.5 inches; three of those days resulted in atrazine detections in the monitoring data. The %SSI for 2007 was 0.15%.

In IL-04, atrazine concentrations also were consistently low in all 3 years (<13 ug/L). Rainfall was near normal in April and July and low in May (~10th %ile) and June (~25th %ile) of 2007. Two rainfall events at or above 1 inch occurred during the planting window; the second rainfall resulted in the highest detection measured at the site during the study (~13 ug/L). The %SSI for 2007 was 0.54%.

IL-08 had atrazine concentrations above 30 ug/L in 2 of the 3 years of monitoring. The highest detection in 2005 was <6ug/L, while 2006 had two separate peaks between 30 and 33 ug/L. In 2007, rainfall was generally at or slightly below the median in all months. The monitoring chemograph in 2007 included several samples greater than 20 ug/L, with the highest detection at 43 ug/L. The concentrations detected at IL-08 in 2007 likely reflect exposures during 'near normal' rainfall. The %SSI for 2007 was 1.88%.

In IN-06, atrazine concentrations were consistently low in all 3 years (<13 ug/L). Rainfall was low (<25th %ile) in April, May, and July of 2007. However, the highest detection (12

ug/L) coincided with a 1.5 inch rainfall event in late April, shortly after the beginning of the planting season. The %SSI for 2007 was 0.39%.

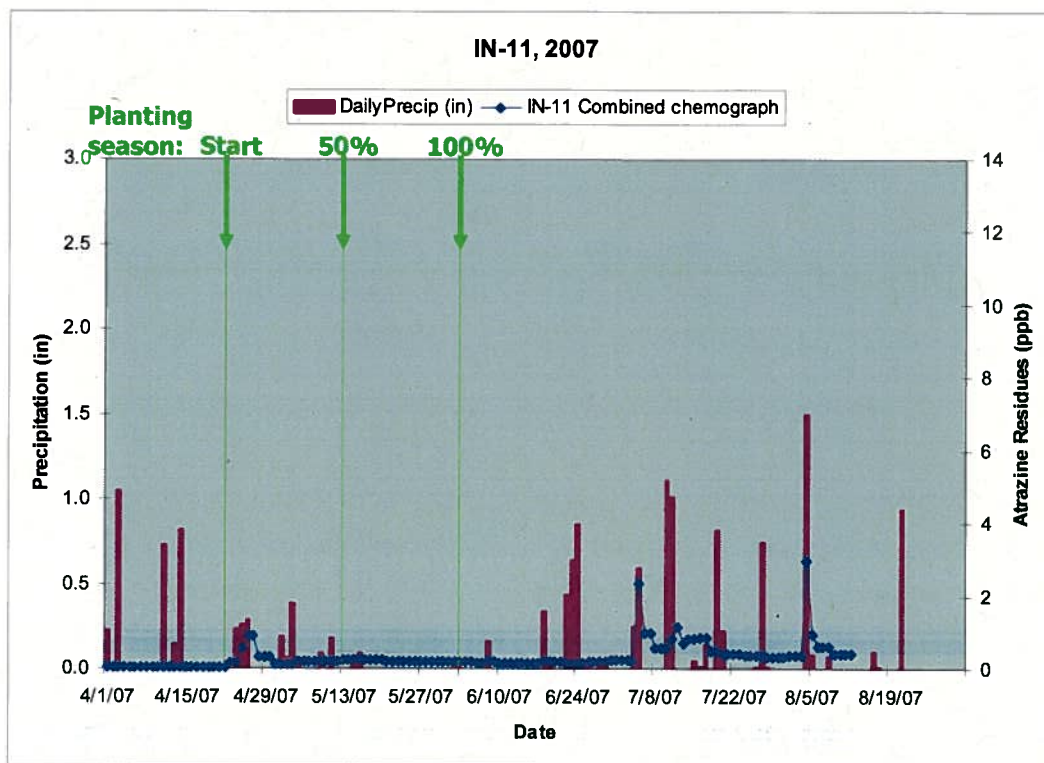
In OH-02, atrazine concentrations were less than 20 ug/L in all 3 years. Rainfall was low (<25th %ile) in April, May, and July of 2007. Overall, the rainfall totals in the April-May window were the lowest of the three years of monitoring. The highest detection (<10 ug/L) in 2007 came from an autosample taken after a mid-May rainfall during the planting season. The %SSI for 2007 was 0.41%.

While monthly rainfall totals at the sites were variable, all of these sites had several rainfall events during the planting season. None of the low-rainfall sites triggered the LOC based on the 4% SSI trigger set with the 2007 version of CASM\_Atrazine.

### **IN-11 – 3rd year of monitoring**

Monitoring continued for a third year at IN-11 based on an exceedance of the LOC in 2005, largely due to a single event (208 ug/L with the grab sample) using a staircase interpolation between sampling events. The site also had low (<25<sup>th</sup> percentile) rainfall totals in 2005 and high (>75<sup>th</sup> percentile) rainfall totals in 2006. Atrazine concentrations did not exceed the LOC in 2006.

Rainfall during the planting period in 2007 was not only the lowest of the three monitoring years, but the rainfall in May was less than the lowest monthly total reported between 1963 and 2001. Most of the April rain (2.9 of 3.7 inches) occurred before planting began (Figure 5). Planting began later in 2007 than in previous years, possibly due to wet fields from early April rains. Rainfall during planting window was low (1.9 inches between 4/22 and 6/3).



**Figure 5 Atrazine concentrations and rainfall amounts for IN-11, 2007**

The low precipitation during the planting window reflects extreme dry conditions for this site, making it difficult for OPP to draw any definitive conclusions regarding the potential for atrazine exposure in the stream during a typical rainfall year. Therefore, OPP believes that an additional year of monitoring at this site is warranted.